Z306 MOLECULAR CONTAMINATION AD HOC COMMITTEE RESULTS

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LDEF external surfaces which did not receive significant amounts of atomic oxygen were observed to be coated with a brown contamination, apparently the result of a condensed organic residue darkened due to UV radiation exposure. During the initial Materials Special Investigation Group (MSIG) Meeting after LDEF deintegration, held in Seattle - July 1990, this organic contamination was the subject of much discussion. The amount of contamination was thought to be significant and its source was immediately believed to be the Z306 black thermal control coating used to coat the entire inner surface of LDEF. Due to the size of the structure, it was not feasible to bake-out the coating. However, initial data on the contamination film was confusing in that significant amounts of silicon was observed by several different researchers. Silicon (from silicone) was not expected to be a potential outgassing product of the Z306 polyurethane coating. To investigate the connection between external contamination and the interior paint, a MSIG ad hoc committee was formed.

Committee Members

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The ad hoc committee's objective was to develop a plan of attack for analysis of the interior paint,which would in turn determine the extent of external contamination induced by its presence. The approach developed to meet the committee objective was defined as the following four tasks. First, we needed as much historical background as possible into the coating used on LDEF and how it was applied. Any test specimens of LDEF-era paint were also of interest. Second, we needed a thorough examination of the contaminant film. Third, we would characterize the specimens of Z306 paint that we could obtain, particularly concentrating of the outgassed condensables. And fourth, we would attempt to duplicate the characteristics of the LDEF contamination by conducting simulated UV exposure of outgassed condensables from Z306 paint.

OBJECTIVE

To Develop And Implement A Test Plan For The Analysis Of LDEF Interior Thermal Control Paint, Determining Possible Connection With The Brown Deposits Found On External Structures

APPROACH

TASK 1. OBTAIN HISTORICAL INFORMATION AND TEST SPECIMENS

TASK 2. CONTAMINANT CHARACTERIZATION

TASK 3. CHARACTERIZATION OF COATINGS AND OUTGASSED CONDENSABLES

TASK 4. SIMULATED UV EXPOSURE OF OUTGASSED CONDENSABLES

Under Task 1, the following information was obtained.

LDEF interior surfaces were painted by a number of different people at different sites. This compounds the difficulty with treating all aspects of the Z306 application issue with certainty.

The standard finish used was a single coat of 9924 wash primer followed by one to four coats of Z306. As an illustration of the different groups involved with painting, MIL-P-23377 epoxy primer has been observed as having been used on some of the experiment trays.

In all cases, those involved with the painting of LDEF structures have indicated that the application of Z306 was conducted strictly in accordance with the vendor specification. This is pertinent information, since there had been some unsubstantiated reports of silicone oil being added to the Z306 to aid in its application. Polyurethanes are extremely sensitive to silicones and their presence will result in coating flaws such as "fisheyes". No documentation concerning the use silicones in Z306 has been obtained.

TASK 1. OBTAIN HISTORICAL INFORMATION AND TEST SPECIMENS

- **Structures Painted By LaRC, By Subcontractors, And By Experimenters (Trays)**
- **Chemglaze 9924 Primer (0.0005 Inch), Followed By Z306 Topcoat (0.0015 to 0.0050 Inch)**

  Note: MIL-P-23377 Epoxy Primer Used On Some Trays
- **Coatings Applied Per Vendor Specification**

Several test specimens were obtained by the ad hoc committee. Fight specimens were obtained from the backs of experiment trays. The difficult specimens to obtain were the specimens which could be used as controls, since the present investigation was not a planned experiment (generally the case with all MSIG investigations). Remarkably, a 6" x 6" witness coupon of Z306 was obtained from the structure painting process. In addition, 1" disks of Z306 that were sprayed at about the same time as LDEF were obtained from NASA LaRC. A section of A0178 thermal control blanket was obtained (these blankets were coated with Z306 on the back). The final control specimens were unsprayed samples of currently available Z306 and 9924 coatings.

TASK 1. OBTAIN HISTORICAL INFORMATION AND TEST SPECIMENS (Continued)

- **Flight Specimens**
  - **Samples From Back Of Trays**
- **Controls**
  - **1 - 6"x6" Panel Of LDEF Coating (Carol Kiser)**
  - **1" Disks With LDEF Era Coating (Wayne Slemp)**
  - **8"x12" Section Of A0178 Thermal Blanket, Flight Control (Dublin Inst., ESA-ESTEC)**
  - **Current Vintage Z306 & 9924 Coatings**

Chemical characterization of the contamination deposit was initially made using IR spectroscopy. The spectra are shown in figures 1-6, and were taken from opposing surfaces on LDEF. With the exception of the spectra taken for the deposit on tray C12, all the IR spectra are remarkably consistent. The spectra indicate O-H, N-H, and C-H stretching absorption bands, as well as carbonyl and silicate type bonds. All of the spectra exhibit 'broadening', indicating that the chemical bonds or groups identified are in varied chemical environments.

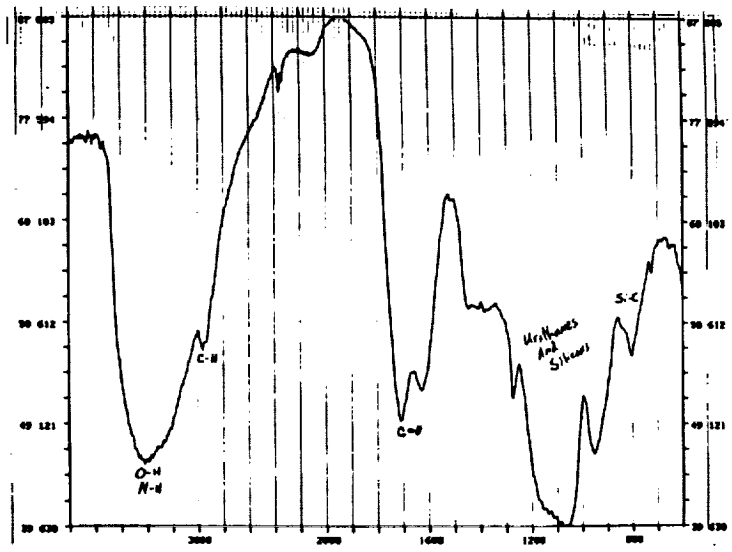
Elemental analysis of the contaminant was made with the use of EDX, shown in figures 7 & 8. Previously reported results of the contaminant at tray C12 have shown that particular deposit to contain phosphorus, a consequence of the outgassing of phosphate esters from the C12 experiment. The EDX for space and earth end deposits do not indicate phosphorus, but do indicate silicon. Trace amounts of chloride and sulfur were also observed.

ESCA was also used by NASA LaRC to characterize the contaminant film. Observations indicate that the silicon portion of the contaminant is generally in silicate form (specimens were from the LDEF leading edge) but some measurements did detect silicone.

At the time of the Materials Workshop, it was agreed that more elemental analysis was needed. Since the Workshop, data obtained by Aerospace Corp on tray D8 indicates the contaminant to contain 28.4% C, 4.1% H, 25.8% O, 18.9% Si, 0.7% N, and trace levels of Cl, F, and P.

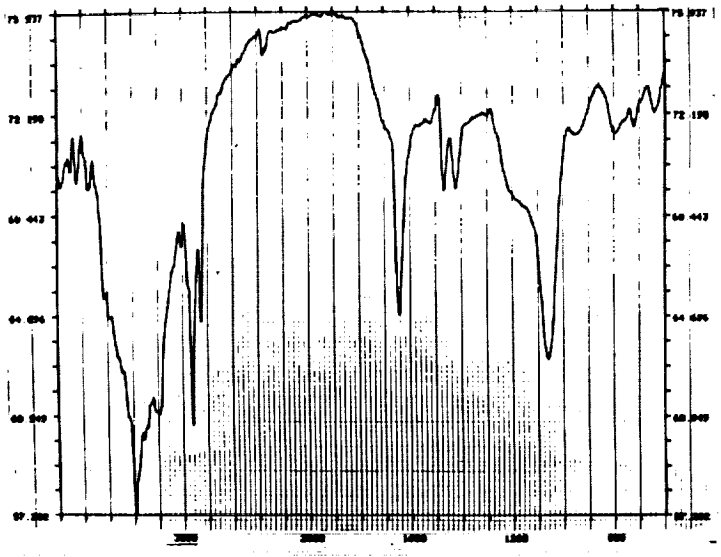
TASK 2. CONTAMINANT CHARACTERIZATION

- **IR Spectroscopy Indicates O-H, N-H, C-H, C=O, And Silicate Bonds In "Broadening" Chemical Environments**
- **Elemental Analysis Indicates Presence of Silicon In General; Phosphorus In Particular Around Tray C12**
- **Silicon Is Generally In Silicate Form, Some Measurements Detect Silicone**
- **Need Better Elemental Analysis**



Space End Brown Film, Longeron 13

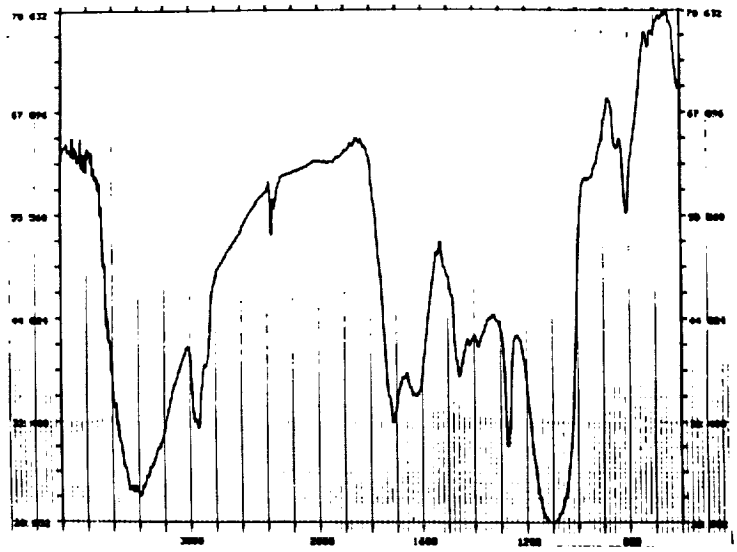
FIGURE 1.



Tray Clamp F12-7: Shim Deposit On Back Surface

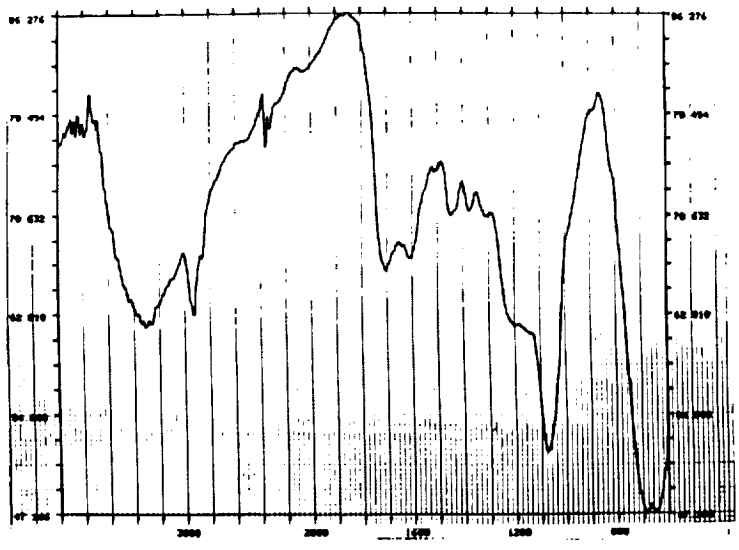
FIGURE 2.

Original figures unavailable at time of publication.



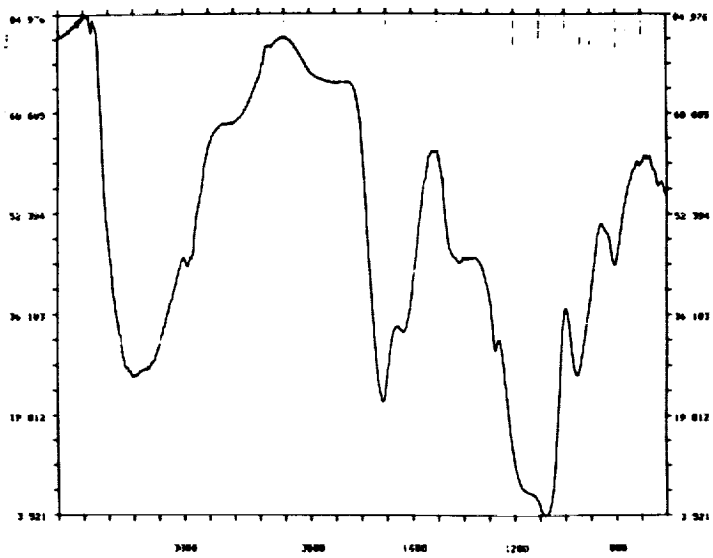
Tray Clamp E06-1: Back Surface Beside Shim, Beveled Edge

FIGURE 3.



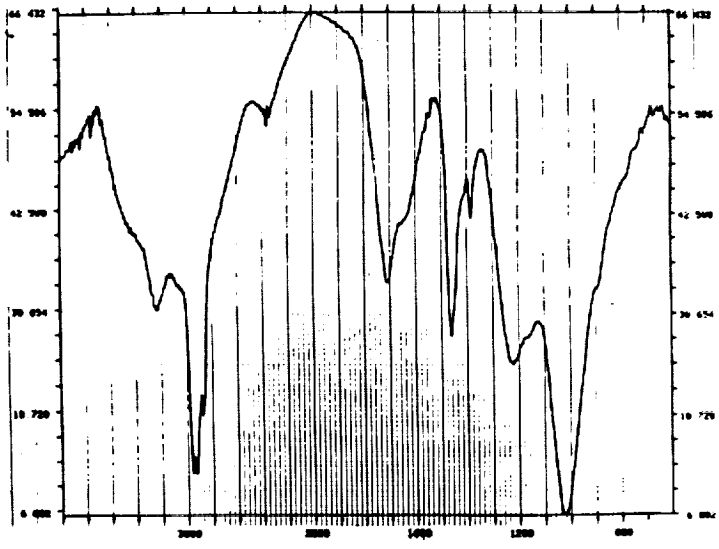
Tray H06: Brown Film On Protected Surface

FIGURE 4.



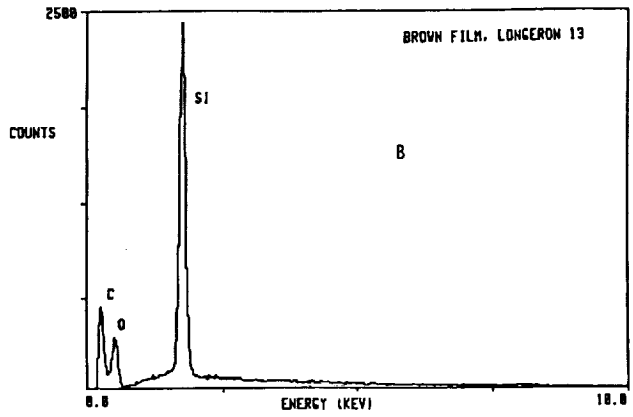
Earth End Frame Brown Film, Beside Tray G12

FIGURE 5.



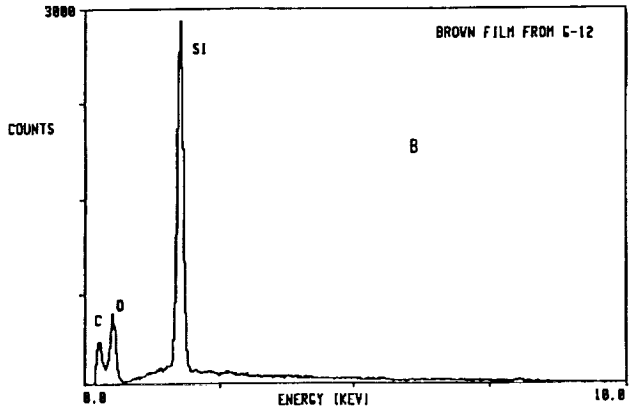
Tray C12: Brown Film

FIGURE 6.



EDX Elemental Survey Of Brown Film, Space End Longeron 13

FIGURE 7.



EDX Elemental Survey Of Brown Film, Earth End Longeron 12

FIGURE 8.

Characterization of the control specimen coatings and outgassed condensables was conducted. IR spectra were obtained for the paint films and are shown in figure 9 (for Z306) and figure 10 (for 9924).

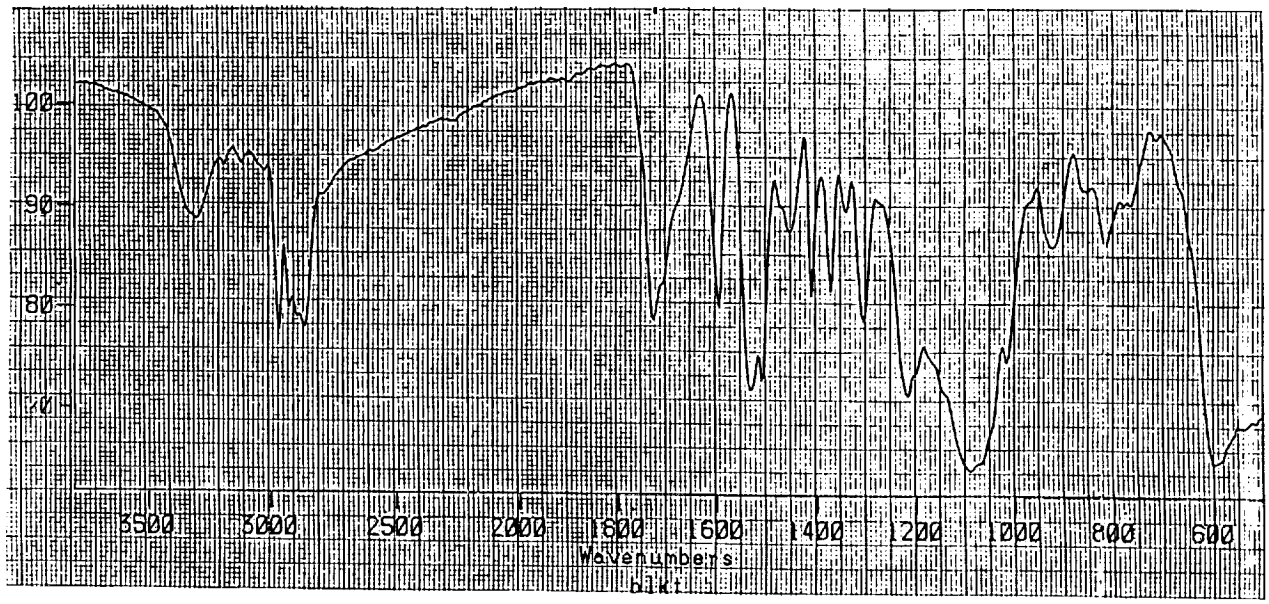
Solvent extractions were also made of the control paint specimens in an attempt to characterize the extractable fractions. Several different solvents were used in the extraction analyses, and the IR spectra resulting from these extractions are shown in figures 11-13. Quantitative measurements of the amounts of extractables in test specimens were measured at JPL. Disk control specimens of LDEF-era Z306 were observed to contain 1-2% extractable aliphatic hydrocarbon, whereas newly painted control specimens contained only 0.1%. Neither of these specimens contained extractable silicone.

Outgassing data of interest to the present analysis is shown in Table 1. Characterization of the collected condensables is shown in figures 14-16. A difference spectra, subtracting the condensables spectra from the paint spectra, is shown in figure 17. The difference spectra is comparable to the spectra for amorphous silica, shown in figure 18. Finally, an IR spectra of the condensables from the thermal blanket velcro adhesive is shown in figure 19.

Cross-sectioning and subsequent chemical analysis of test specimens was conducted. On an LDEF flight specimen thermal blanket, silicone was detected on the surface. Cross-sections of paint specimens showed silicon throughout the paint film, but this is in the form of silicate used as part of the paint pigment package.

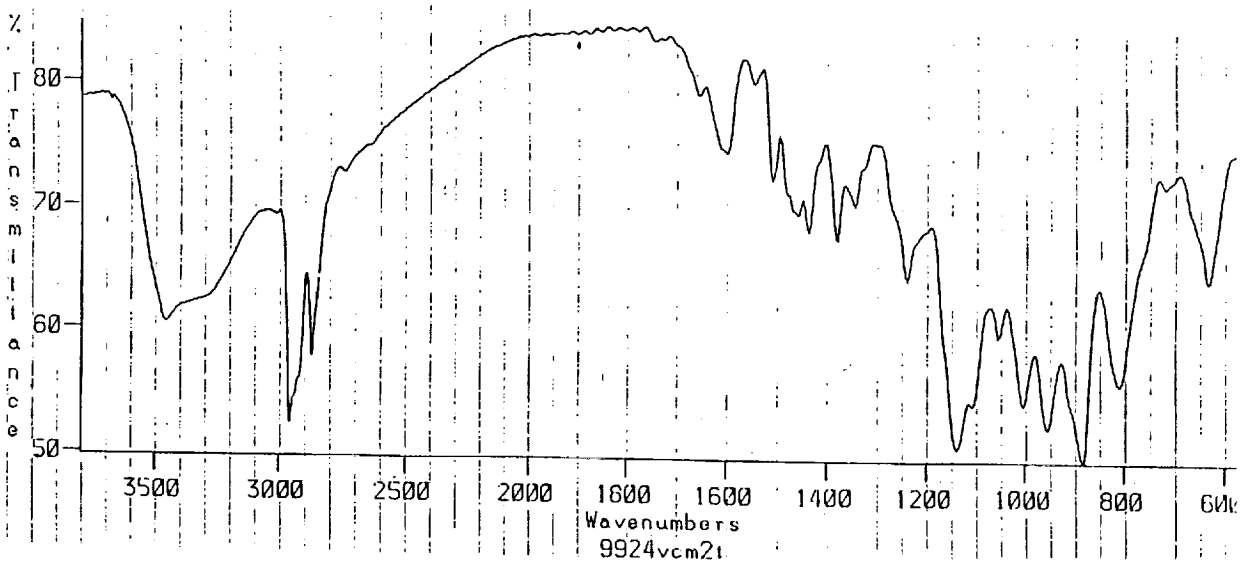
TASK 3. CHARACTERIZATION OF COATINGS AND OUTGASSED CONDENSABLES

- **IR Spectroscopy Of:**
  - **Paints Themselves**
  - **Solvent Extractions**
    - **Methylene Chloride, MEK, Petroleum Ether, Hexane, THF Used**
    - **1 - 2% Extractable Aliphatic HC In Disk Control Specimens**
    - **0.1% In Newly Painted Controls**
  - **Collected Condensables**
- **Cross-Section And Elemental Analysis**
  - **Silicone At Surface Of Thermal Blanket Coatings (LDEF Flight Specimen)**
  - **Silicon Observed Throughout Paint Films**



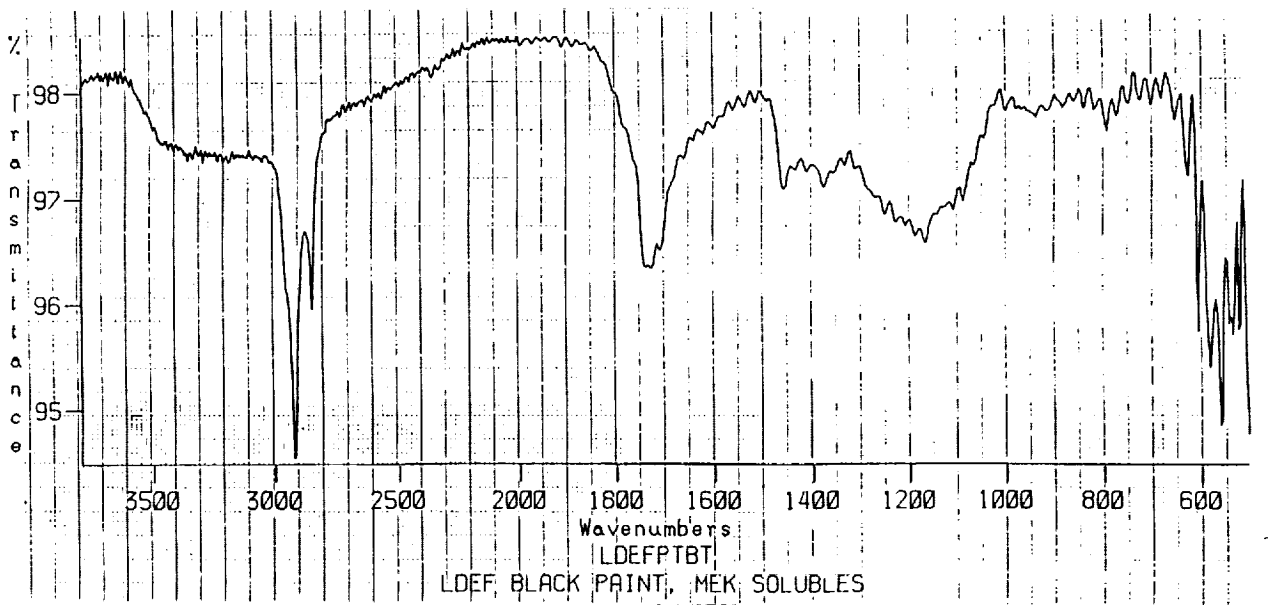
Chemglaze Z306 Thermal Control Paint

FIGURE 9.



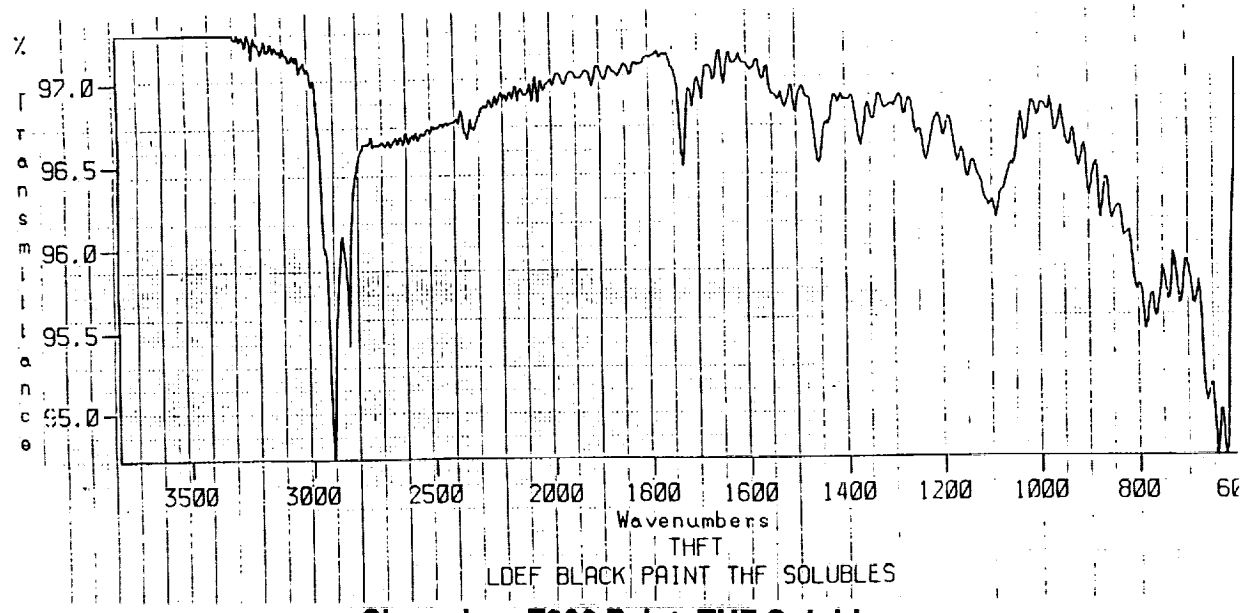
Chemglaze 9924 Primer

FIGURE 10.



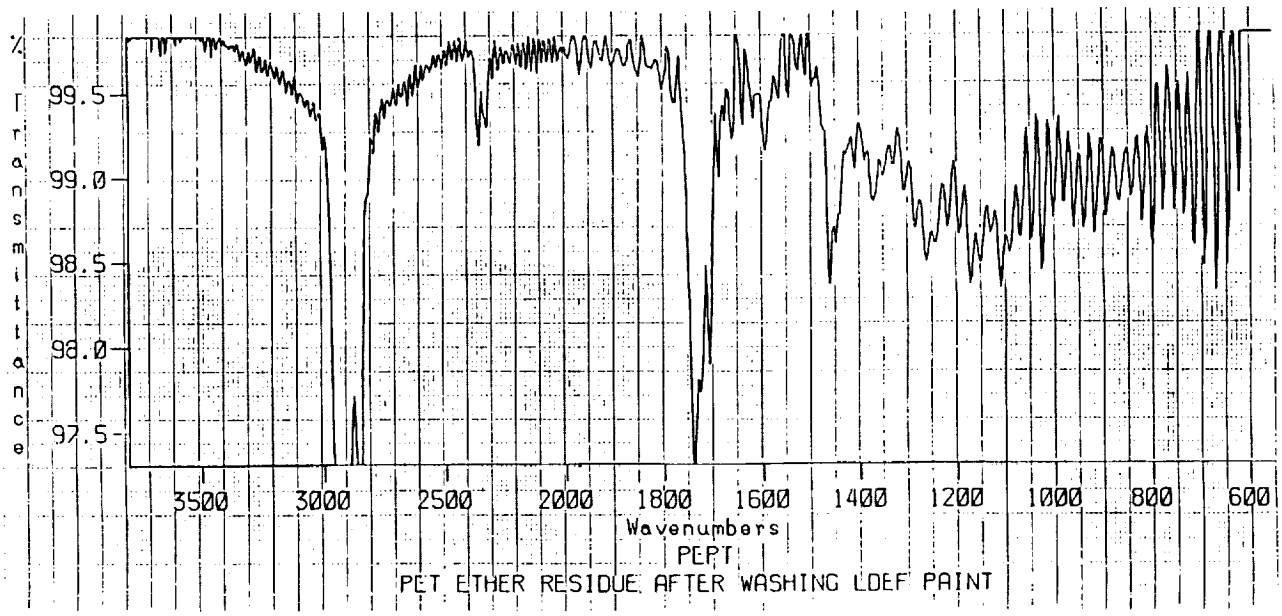
Chemglaze Z306 Paint, MEK Solubles

FIGURE 11.



Chemglaze Z306 Paint, THF Solubles

FIGURE 12.



Chemglaze Z306 Paint, Petroleum Ether Solubles

FIGURE 13.

Outgassing data indicates that the primers are significant sources of condensable materials. All data measured by the committee is for a seven day outgassing period, rather than the 24 hours used in the standard outgassing test (NASA SP-R-0022A). Comparison is also made to available literature data, which used the standard outgassing period.

TABLE 1.

RESEARCH & ENGINEERING

Z306 MOLECULAR CONTAMINATION AD HOC COMMITTEE RESULTS

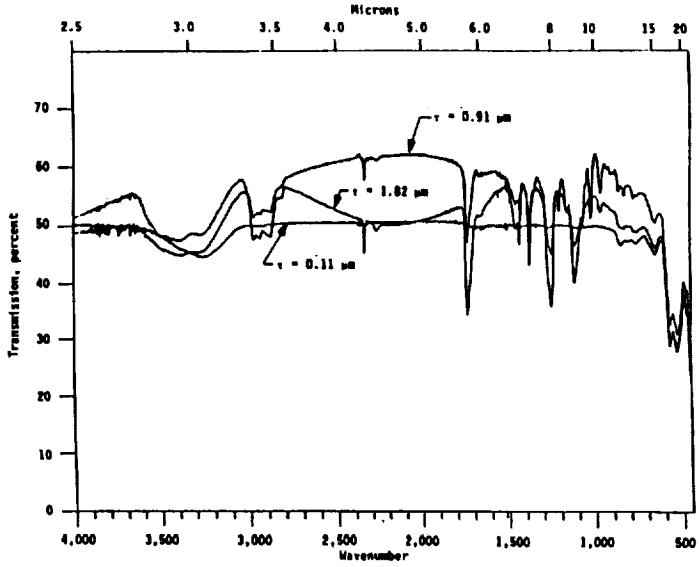
Boeing Defense & Space Group

OUTGASSING DATA

MATERIAL	TML	VCM
Z306	1.08%	0.04% (0.03%)[1]
9924	10.2%	0.14%
Z306+9924	4.13%	0.06% (0.07%)[1]
MIL-P-23377	2.36%	0.11%
A0178 RTV ADHESIVE (7 DAY OUTGASSING)	(0.22%)[2] 0.53%	(0.02%)[2] 0.06%

1 A.P.M. Glassford, Lockheed M&S (1978)
2 MSFC-HDBK-527F, 24 Hour Outgassing (1988)

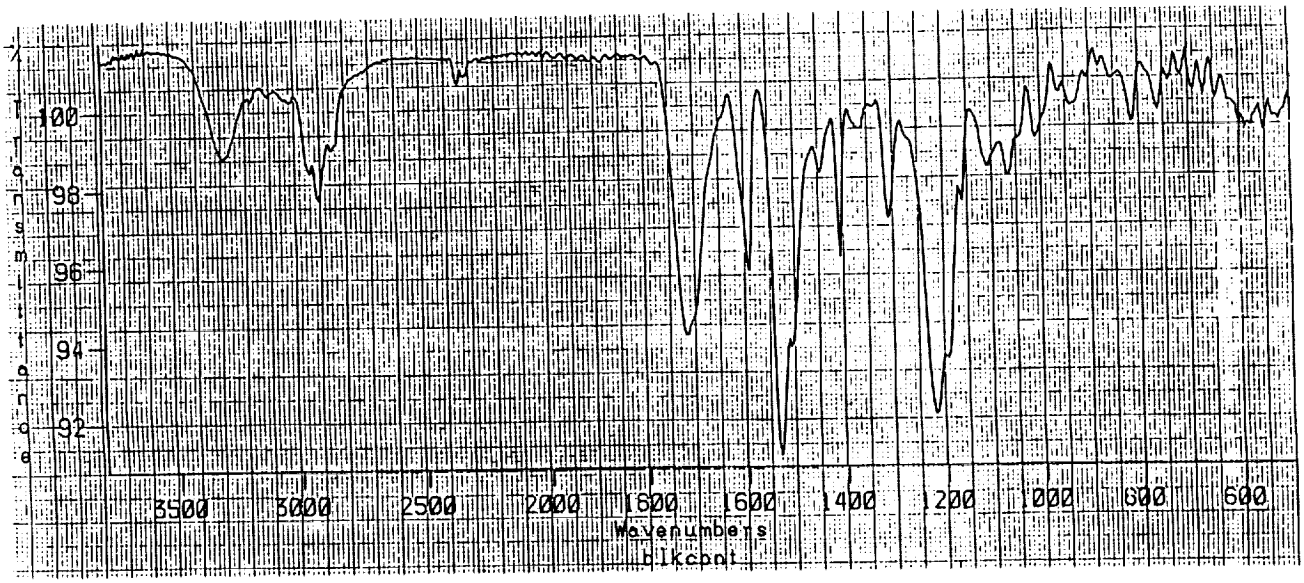
IR spectra of condensed outgassing contaminants from Z306 was obtained by Wood, et al., for three film thicknesses.



B.E. Wood, et al., Surface Effects of Satellite Material Outgassing Products, AEDC-TR-89-2, p.33, June 1989

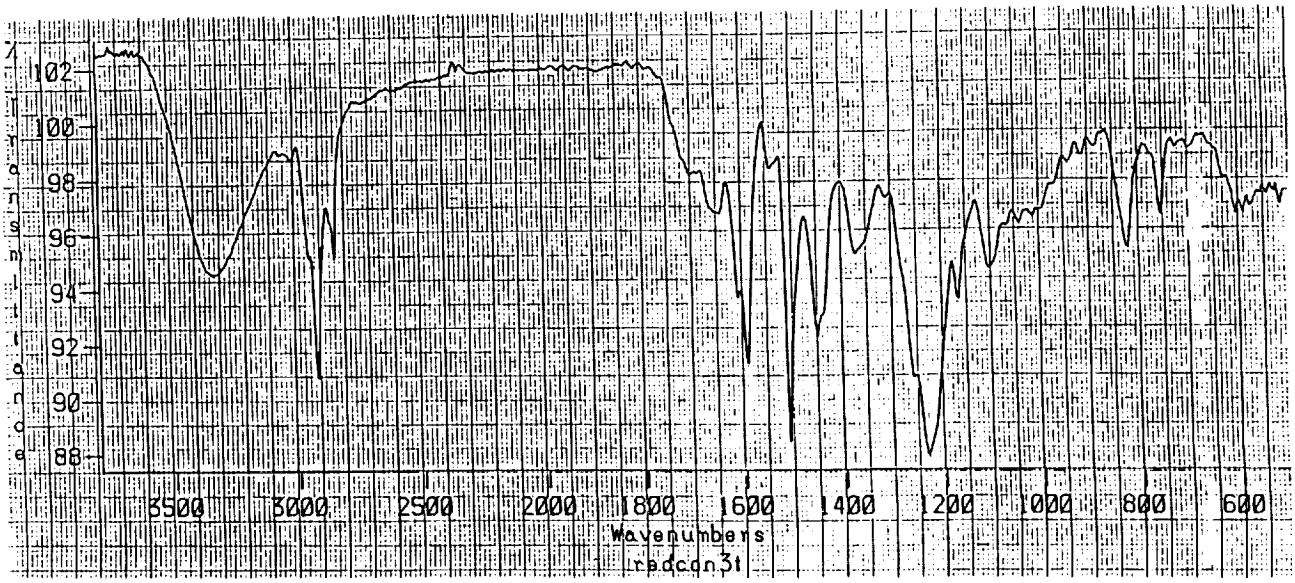
FIGURE 14.

Condensables from Z306 were all apparently removed with MEK. The solvent was used to transfer the condensate to a salt window, and was then allowed to evaporate prior to measuring the IR spectrum for the condensate. A following rinse of the condensate collector plate with petroleum ether, a good solvent for silicones, did not yield a spectrum.



MEK Wash Of Z306 Condensables

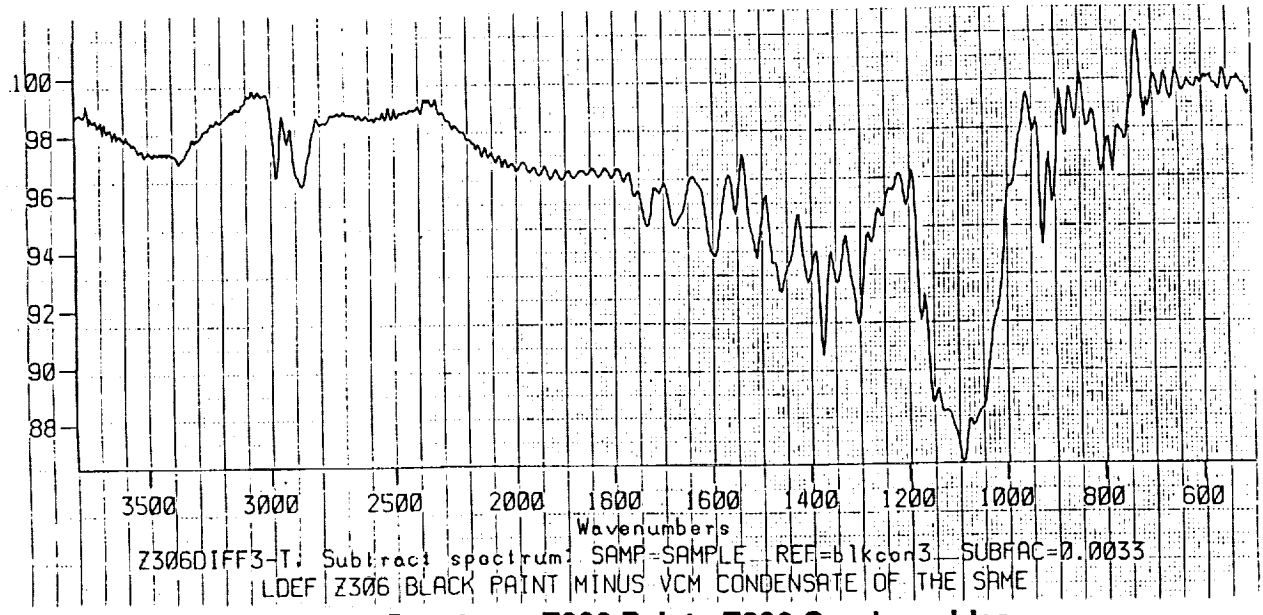
FIGURE 15.



MEK Wash Of 9924 Condensables

FIGURE 16.

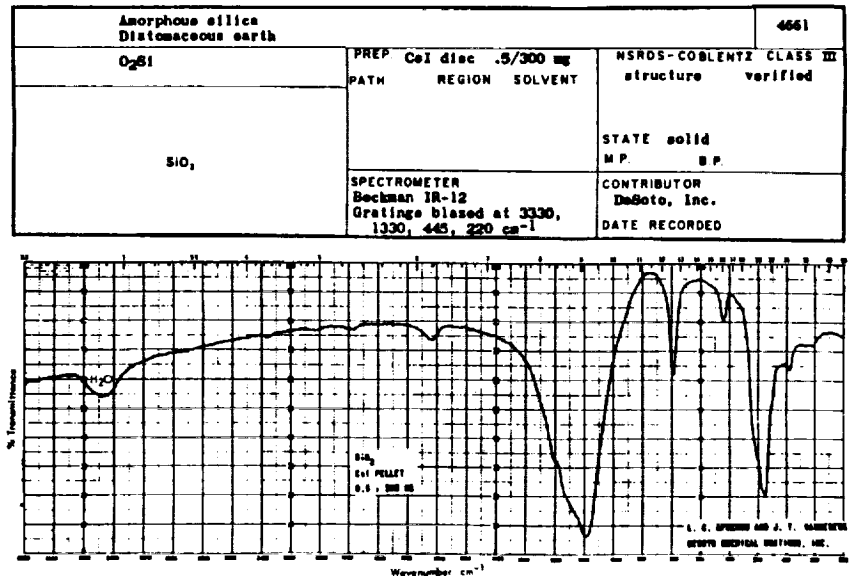
The principal difference between the Z306 paint and its condensables is the silicate absorption band at 1100 wavenumbers. Silicate materials are common fillers or extenders used in paint pigments.



Difference Spectrum, Z306 Paint - Z306 Condensables

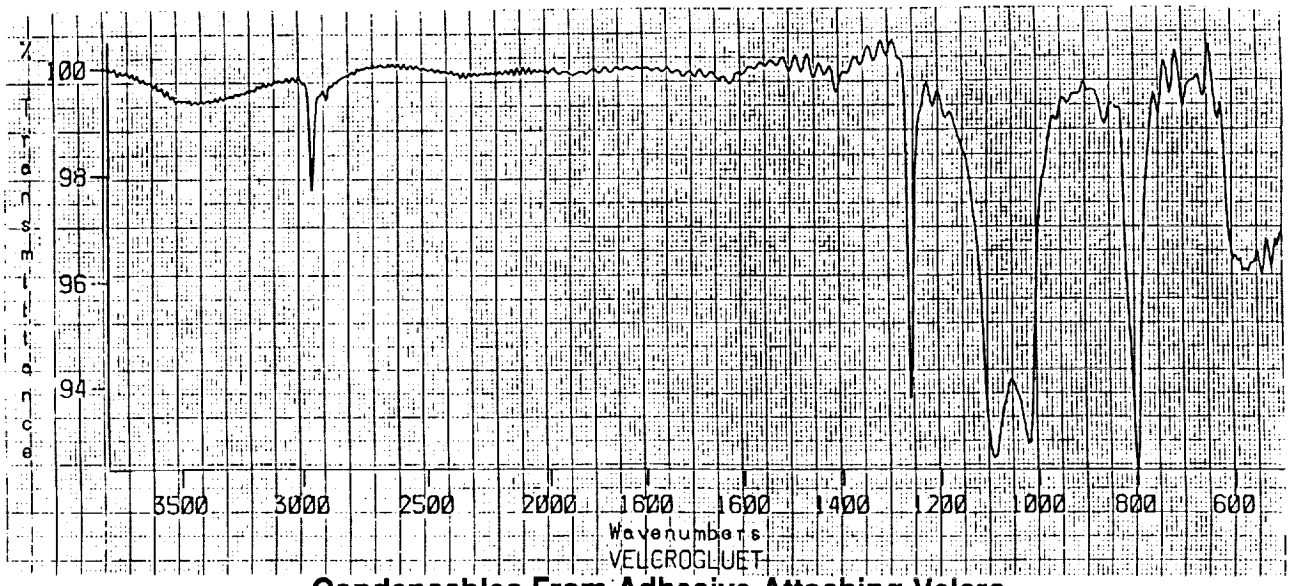
FIGURE 17.

Example IR spectra of amorphous silica, obtained from a paint coatings supplier.



Amorphous Silica Spectrum

FIGURE 18.



Condensables From Adhesive Attaching Velcro To A0178 Thermal Blanket, Flight Control Specimen

FIGURE 19.

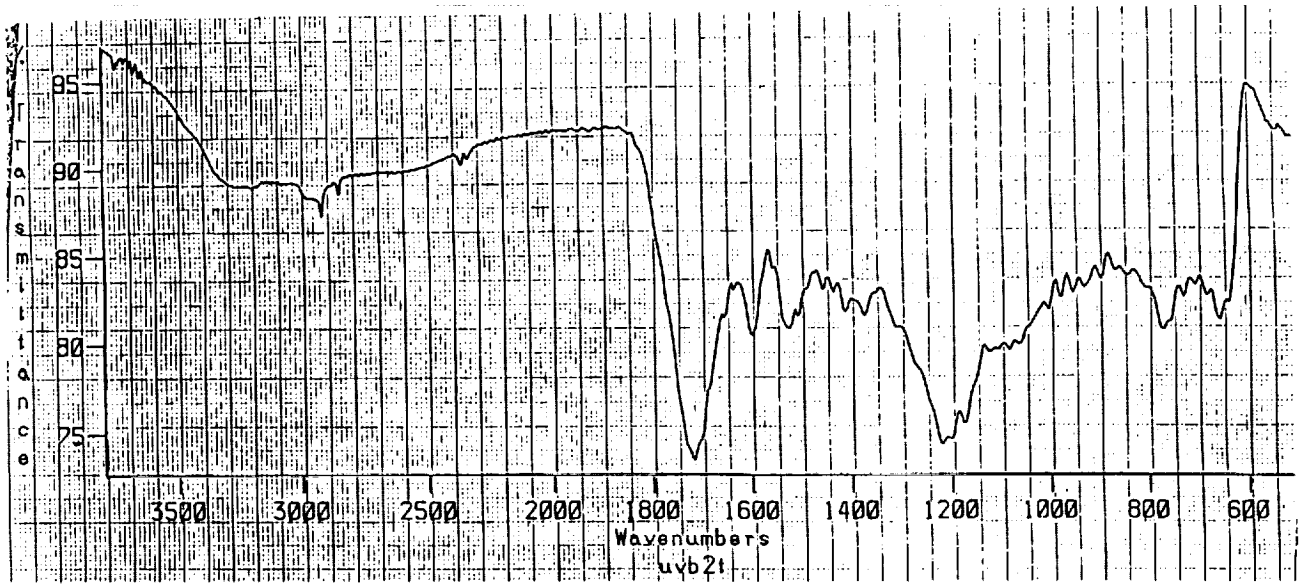
The final ad hoc committee task was an attempt to form the contaminant film observed on LDEF surfaces through the simulated UV environment exposure of Z306 condensables. This task was conducted in two parts. First, condensables were irradiated with a low power UV source in air. The results are shown in figure 20. Broadening of the IR absorption peaks was accomplished (compare to figure 14), indicating that the condensable material is being modified and the primary functional groups are being influenced in several ways due to a varied chemical environment. A similar effect is noted for the 9924 primer in figure 21.

The second part of task 4 was to use the optics degradation simulation chamber at Arnold Engineering Development Center. Z306 paint was outgassed onto a germanium collector plate, where the condensables could be irradiated with simulated UV radiation at one-sun intensity for 200 hours. The germanium plate was subsequently removed and the spectra of figure 22 obtained. A spectra of the space end brown film contaminant is shown in figure 23 for comparison.

An interesting comparison of the the LDEF contaminant can be made with the UV photodeposited silicone oil shown in figure 24.

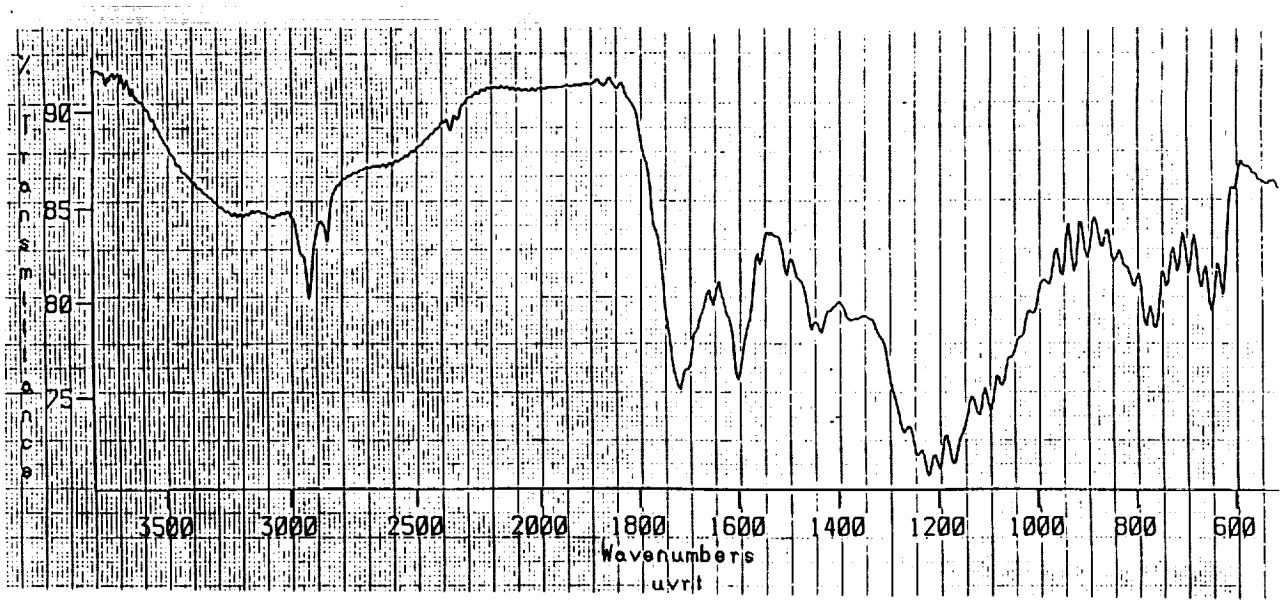
TASK 4. SIMULATED UV EXPOSURE OF OUTGASSED CONDENSABLES

- **IR Spectroscopy Of Condensables Irradiated In Air With 254nm UV Source (3.3 W/sq. m)**
- **IR Spectroscopy Of Condensables At AEDC**



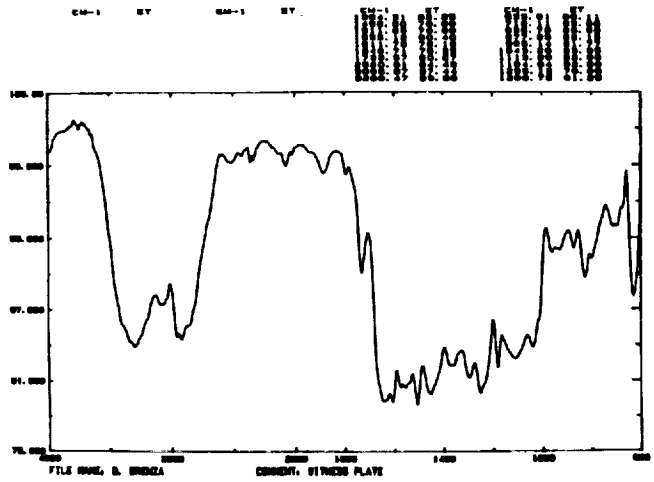
Chemglaze Z306 Condensables After UV Exposure In Air

FIGURE 20.



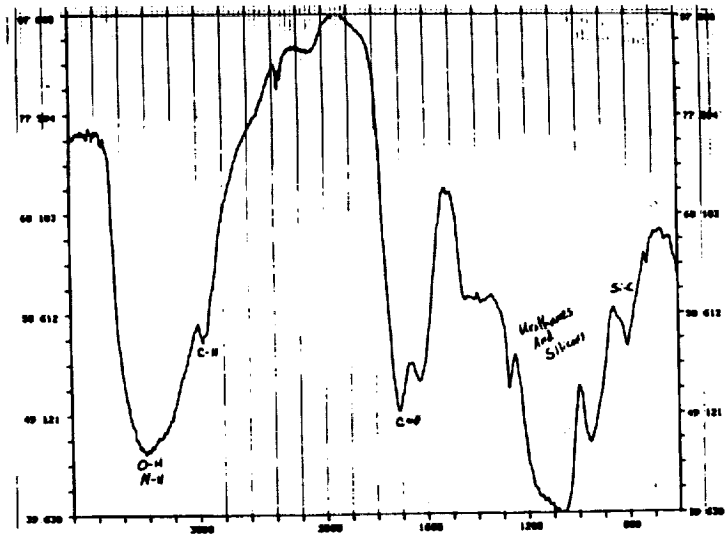
Chemglaze 9924 Condensables After UV Exposure In Air

FIGURE 21.



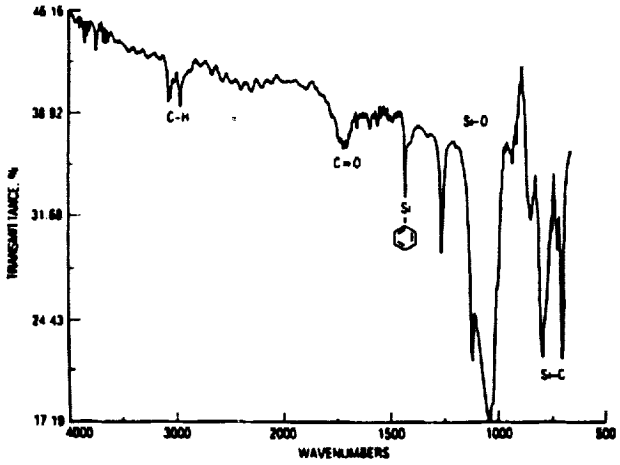
UV-Irradiated Z306+9924 Outgassing Film (AEDC)

FIGURE 22.



Space End Brown Film, Longeron 13

FIGURE 23.



UV Photodeposit of DC-704 Silicone Oil, T. B. Stewart, et al., Photolysis Of Spacecraft Contaminants, The Aerospace Corp., SD-TR-89-45, July 1989

FIGURE 24.

CONCLUSIONS

Several conclusions were drawn by the Z306 molecular contamination ad hoc committee. Conclusions can be made about the contaminant film. The contaminant, with the most notable exception of the area around tray C12, is consistent in IR spectra from opposite sides and ends of LDEF. This contaminant contains several organic functional groups in varied chemical environments, and also contains silicon, principally in silicate form when it can react with atomic oxygen.

Outgassing and extraction measurements indicate that the Z306, and especially its primer, are significant sources of molecular contamination. Many characteristics of the contaminant film can be attributed to paint condensables by comparing IR spectra. However, no evidence could be found that the paint coatings are a source of silicone contamination.

UV irradiation of outgassed condensables from Z306 produced some characteristics of the IR spectra obtained with LDEF contamination. What is lacking, however, is a source of the significant levels of silicon detected in the contaminant film.

Therefore, silicones from other sources, in addition to the outgassing from the Z306 and the primers used, were the primary contributors to the molecular contamination observed on LDEF.

CONCLUSIONS

- **Spectroscopic Evidence Indicates LDEF Contamination Films Contain Silicon, Principally In Silicate Form, And Several Organic Functional Groups In Varied Chemical Environments**
- **Z306 And Its Primer (9924 Or MIL-P-23377) Are Significant Sources Of Molecular Contamination, But Not Of Silicone Contamination**
- **UV-Irradiation Of Outgassed Condensables From Z306 Produces Some But Not All Of The Characteristics Exhibited By LDEF Molecular Contamination**
- **Silicones, Z306, And Primer Were The Primary Contributors To The Observed Molecular Contamination On LDEF**

POINTS OF INTEREST

To stimulate further thought on the subject of the LDEF molecular contamination, several points of interest can be raised which were discussed by the committee during its investigations.

The first point concerns the source of silicon which has been observed in the LDEF molecular contamination film. Since the committee was not able to determine that Z306 was the source of the silicon, what other sources might there be? One source would be the silicone adhesive that was used for bonding velcro tape to thermal control blankets. The amount of adhesive used for this purpose has been estimated at more than 3 kilograms. This is not intended as a criticism of the particular experiments or experimenters which used this bonding system. Many other potential sources of silicone have been identified on LDEF. The point is that the silicone had to come from somewhere, and the cumulative silicone adhesive and potting compounds used on LDEF must be the source.

Finally, the relative uniformity in the IR spectra obtained for contaminant films from various LDEF surfaces leads to either, and perhaps both, of the following two points. One possibility is that the contaminant film has reached a chemical equilibrium with the LEO environment, essentially achieving environmental stability. The other possibility is that the contamination mechanism that produced these films was not line-of-sight, suggesting a significant departure from the classical contamination control design approach.

POINTS OF INTEREST

- **Silicone Adhesive Used For Bonding Velcro Tape To Thermal Blankets**
  - **Estimate 2 g Adhesive/Tape, 2 Tapes/Attachment, 48 Attachments/Tray, 17 Trays**
  - **Yields >3 kg Silicone Adhesive**
- **Numerous Potential Sources Of Silicone Contamination Have Been Identified**
- **Relatively Uniform Spectra For Contaminant Films From Various Location Indicates:**
  - **Equilibrium Chemistry In Contamination Products (Environmental Stability)**
  - **Non Line-Of-Sight Contamination Mechanisms**